

What is claimed is:

1. An analytical apparatus to monitor fluid systems, comprising:
 - at least one extraction module having a raw-sample reservoir
 - 5 connected by input fluid conduit to individual ones of said fluid systems, to extract raw samples for analysis from said fluid systems;
 - one or more modification modules comprising additive materials to modify the extracted raw samples prior to analysis;
 - an analytical device to receive at least a portion of said raw samples in
 - 10 an ordered sequence, and to determine concentration of at least one constituent of said sample portion;
 - fluid-handling apparatus for transferring fluid through the analytical apparatus; and
 - a computerized control and management system to manage operations
 - 15 of component modules and devices, and to report analytical results;
 - characterized in that the control and management system coordinates extraction of raw samples, modification as needed, introduction of fluids to the analytical device, and reporting of analytical results on a continuous basis over plural cycles.
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2. The analytical apparatus of claim 1 comprising a plurality of extraction modules associated one-to-one with a like plurality of fluid systems.
3. The analytical apparatus of claim 1 wherein the fluid systems are wet baths
- 25 in a processing environment, and the extracted fluids are liquids.
4. The analytical apparatus of claim 3 wherein the processing environment is a fabrication system (fab) devoted to semiconductor integrated circuit (IC) manufacturing.
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5. The analytical apparatus of claim 3 wherein the modification modules comprise chemicals for altering pH of extracted liquids.

6. The analytical apparatus of claim 3 wherein the analytical device is a mass spectrometer, and further comprising an ionization apparatus for vaporizing and ionizing liquids prior to introduction to the mass spectrometer.

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7. The analytical apparatus of claim 6 wherein analysis is based on isotopic ratio, the one or more modification modules comprise isotope dilution modules for introducing isotope mixtures to liquids in the system, and the isotope mixtures are in a ratio not naturally occurring.

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8. The analytical apparatus of claim 1 comprising a plurality of extraction modules and a plurality of modification modules, wherein the fluid-handling apparatus comprises one or more mixers having two or more inputs to one output, and switching valves between the modules and the inputs to the mixers, and wherein the control and management system cycles the switching valves and causes movement of liquids, and of materials from the modification modules, to mix selected liquids with selected materials from the modification modules.

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9. The analytical apparatus of claim 8 wherein individual ones of the mixers comprise conduit junctions having two or more input conduits feeding one output conduit, with the conduit paths arranged to provide for laminar flow and substantial direction change to influence mixing.

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10. The analytical apparatus of claim 3 wherein the raw-sample reservoir in the at least one extraction module is connected to a vacuum apparatus through a remotely-operable valve, to draw a relative vacuum in the reservoir to draw material from the fluid system connected by conduit to the reservoir.

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11. The analytical apparatus of claim 10 wherein the raw-sample reservoir is vertically-oriented and the conduit from the wet-bath enters at a height on the

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reservoir such that a liquid sample drawn into the reservoir may have a gas gap over the sample.

12. The analytical apparatus of claim 11 further comprising a cover-gas
5 source connected to the sample reservoir through a remotely-operable valve to provide a cover gas over a raw sample in the reservoir.

13. The analytical apparatus of claim 12 wherein the cover gas is nitrogen.

10 14. The analytical apparatus of claim 11 further comprising a syringe connected by intermediate conduit to the sample reservoir at a height on the reservoir to enter beneath the surface of a sample in the reservoir, such that withdrawing a plunger of the syringe by a precise distance draws a precise volume of the raw sample in the reservoir into the syringe.

15 15. The analytical apparatus of claim 14 wherein the syringe comprises a plunger driven by the control and management system through a precision translation mechanism, enabling precision volume control.

20 16. The analytical apparatus of claim 15 wherein the control and management system is enabled to vary rate of plunger translation.

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16. The analytical apparatus of claim 15 wherein the precision translation mechanism comprises a precision stepper motor.

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17. The analytical apparatus of claim 14 wherein the syringe is connected through a three-way switching valve to the intermediate conduit to the sample reservoir and to an output conduit to provide the precise volume sample to other elements of the analytical apparatus.

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18. The analytical apparatus of claim 14 further comprising a flush reservoir connected through additional valves to the syringe to the raw-sample

reservoir, to a source of flushing liquids, to a second vacuum source, to a cover-gas source, and to a drain line, such that the elements of the extraction module may be flushed and cleaned between sample cycles.

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19. The analytical apparatus of claim 3 wherein individual ones of the modification modules are chemical alteration modules comprising at least one chemical reservoir having a solution of precisely compounded chemicals and apparatus for providing portions of the solution to other elements of the analytical apparatus.

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20. The analytical apparatus of claim 19 wherein the apparatus for providing portions of the solution comprises a syringe connected by intermediate conduit to the chemical reservoir in a manner to enter beneath the surface of solution in the reservoir, such that withdrawing a plunger of the syringe by a precise
15 distance draws a precise volume of the solution in the chemical reservoir into the syringe.

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21. The analytical apparatus of claim 20 wherein the syringe comprises a plunger driven by the control and management system through a precision
20 translation mechanism, enabling precision volume control.

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22. The analytical apparatus of claim 21 wherein the control and management system is enabled to vary rate of plunger translation.

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25 22. The analytical apparatus of claim 21 wherein the precision translation mechanism comprises a precision stepper motor.

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30 23. The analytical apparatus of claim 20 wherein the syringe is connected through a three-way switching valve to the conduit to the chemical reservoir and to an output conduit to provide the precise volume sample to other elements of the analytical apparatus.

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24. The analytical apparatus of claim 20 wherein the portions provided to other elements are provided through a mixer having two or more inputs to one output, with one input connected to the chemical alteration module and another connected to another module in the analytical apparatus.

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25. The analytical apparatus of claim 24 wherein individual ones of the mixers comprise conduit junctions having two or more input conduits feeding one output conduit, with the conduit paths arranged to provide for laminar flow and substantial direction change to influence mixing.

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26. The analytical apparatus of claim 7 wherein individual ones of the isotope dilution modules comprise at least one isotope reservoir containing a mixture of isotopes of a specie to be evaluated, the mixture of isotopes at a ratio not naturally occurring, and a mechanism to provide a portion of the mixture to other elements of the analytical apparatus.

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27. The analytical apparatus of claim 26 wherein the mechanism for providing portions of the solution comprises a syringe connected by intermediate conduit to the isotope reservoir below a surface of the mixture in the reservoir, such that withdrawing a plunger of the syringe by a precise distance draws a precise volume of the mixture in the isotope reservoir into the syringe.

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28. The analytical apparatus of claim 27 wherein the syringe comprises a plunger driven by the control and management system through a precision translation mechanism, enabling precision volume control.

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29. The analytical apparatus of claim 28 wherein the control and management system is enabled to vary rate of plunger translation.

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29. The analytical apparatus of claim 28 wherein the precision translation mechanism comprises a precision stepper motor.

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30. The analytical apparatus of claim 27 wherein the syringe is connected through a three-way switching valve to the conduit to the isotope reservoir and to an output conduit to provide the precise volume sample to other elements of the analytical apparatus.

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31. The analytical apparatus of claim 26 wherein the portions provided to other elements are provided through a mixer having two or more inputs to one output, with one input connected to the chemical alteration module and another connected to another module in the analytical apparatus.

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32. The analytical apparatus of claim 31 wherein individual ones of the mixers comprise conduit junctions having two or more input conduits feeding one output conduit, with the conduit paths arranged to provide for laminar flow and substantial direction change to influence mixing.

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33. The analytical apparatus of claim 27 wherein the isotope reservoir contains an isotope mixture in a solvent at a specific concentration, and further comprising a solvent reservoir in addition to the at least one isotope reservoir, the solvent reservoir containing the solvent common to the isotope mixture in the isotope reservoir, and a system of syringes, connecting conduits and mixers, enabling portions of the isotope mixture to be diluted to lesser concentrations before being provided to other elements of the analytical apparatus.

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34. The analytical apparatus of claim 33 wherein the isotope reservoir holds an isotope mixture in a concentration of 1 part isotope in one million parts of the mixture (1ppm), and the system of syringes, connecting conduits and mixtures enables dilution of six orders of magnitude to one part per trillion (1ppt).

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a vacuum source connected to the raw sample reservoir through a remotely-controllable valve, to draw raw samples into the reservoir; and

a syringe connected by intermediate conduit through a switching valve to the sample reservoir at a height on the reservoir to enter beneath the surface of a sample in the reservoir, and to an ejection conduit, such that withdrawing

a plunger of the syringe by a precise distance draws a precise volume of the raw sample in the reservoir into the syringe, and appropriately switching the valve and extending the plunger ejects the precise volume through the ejection conduit.

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40. The extraction module of claim 39 wherein the raw-sample reservoir is vertically-oriented and the conduit from the liquid systems enters at a height on the reservoir such that a liquid sample drawn into the reservoir may have a gas gap over the sample.

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41. The extraction module of claim 39 further comprising a cover-gas source connected to the sample reservoir through a remotely-operable valve to provide a cover gas over a raw sample in the reservoir.

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42. The extraction module of claim 41 wherein the cover gas is nitrogen.

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43. The extraction module of claim 39 wherein the syringe comprises a plunger with a precision translation mechanism drivable by a control and management system, enabling precision volume control.

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44. The extraction module of claim 43 wherein the precision translation mechanism is controllable at variable translation rates, enabling variation of fluid transfer rate.

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45. The extraction module of claim 43 wherein the precision translation mechanism comprises a precision stepper motor.

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46. The extraction module of claim 39 further comprising a flush reservoir connected through additional valves to the syringe, to the raw-sample reservoir, to a source of flushing liquids, to a second vacuum source, to a cover-gas source, and to a drain line, such that the elements of the extraction module may be flushed and cleaned between sample cycles.

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47. In an analytical apparatus to monitor liquid systems, the apparatus having modules for extracting samples, modifying the samples, and analyzing the samples for concentration of specific constituents, a chemical alteration
5 module comprising:

a chemical reservoir having a solution of precisely compounded chemicals; and

apparatus for providing portions of the solution to other elements of the analytical apparatus.

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48. The chemical alteration module of claim 47 wherein the apparatus for providing portions of the solution comprises a syringe connected by intermediate conduit to the chemical reservoir in a manner to enter beneath the surface of solution in the reservoir, such that withdrawing a plunger of the
15 syringe by a precise distance draws a precise volume of the solution in the chemical reservoir into the syringe.

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49. The chemical alteration module of claim 48 wherein the syringe comprises a plunger having a precision translation mechanism drivable by a
20 control and management system, enabling precision volume control.

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50. The chemical alteration module of claim 49 wherein rate of translation of the precision translation mechanism is variable, enabling variation of rate of liquid transfer.

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51. The chemical alteration module of claim 49 wherein the precision translation mechanism comprises a precision stepper motor.

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52. The chemical alteration module of claim 48 wherein the syringe is
30 connected through a three-way switching valve to the conduit to the chemical reservoir and to an output conduit to provide the precise volume sample to other elements of the analytical apparatus.

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53. In an analytical apparatus to monitor liquid systems, the apparatus having modules for extracting samples, modifying the samples, and analyzing the samples for concentration of specific constituents, an isotope dilution
5 modification module comprising:

at least one isotope reservoir containing a mixture of isotopes of a specie to be evaluated, the mixture of isotopes at a ratio not naturally occurring; and

a mechanism to provide a portion of the mixture to other elements of
10 the analytical apparatus.

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54. The isotope dilution module of claim 53 wherein the mechanism for providing portions of the solution comprises a syringe connected by intermediate conduit to the at least one isotope reservoir below a surface of the
15 mixture in the reservoir, such that withdrawing a plunger of the syringe by a precise distance draws a precise volume of the mixture in the isotope reservoir into the syringe.

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55. The isotope dilution module of claim 54 wherein the syringe comprises a
20 plunger having a precision translation mechanism drivable by a control and management system, enabling precision volume control.

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56. The isotope dilution module of claim 55 wherein the control and management system is enabled to vary rate of plunger translation.
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57. The isotope dilution module of claim 55 wherein the precision translation mechanism comprises a precision stepper motor.

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58. The isotope dilution module of claim 54 wherein the syringe is connected
30 through a three-way switching valve to the conduit to the isotope reservoir and to an output conduit to provide the precise volume sample to other elements of the analytical apparatus.

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59. The isotope dilution module of claim 54 wherein the isotope reservoir contains an isotope mixture in a solvent at a specific concentration, and further comprising a solvent reservoir in addition to the at least one isotope reservoir, the solvent reservoir containing a solvent common to the isotope mixture in the isotope reservoir, and a system of syringes, connecting conduits and mixers, enabling portions of the isotope mixture to be diluted to lesser concentrations before being provided to other elements of the analytical apparatus.

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60. The isotope dilution module of claim 59 wherein the isotope reservoir holds an isotope mixture in a concentration of 1 part isotope in one million parts of the mixture (1ppm), and the system of syringes, connecting conduits and mixtures enables dilution of six orders of magnitude to one part per trillion (1ppt).

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61. The isotope dilution module of claim 60 wherein the syringes in the system of syringes comprises individual syringes each having a plunger, such that withdrawing the plunger of the syringe by a precise distance draws a precise volume of the mixture in the isotope reservoir into the syringe.

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62. The isotope dilution module of claim 61 wherein the syringe comprises a plunger having a precision translation mechanism drivable by the control a management system, enabling precision volume control.

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63. The isotope dilution module of claim 62 wherein the precision translation mechanism comprises a precision stepper motor.

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64. The isotope dilution module of claim 59 wherein individual ones of the syringes in the system of syringes are connected by switching valves to individual inputs to a mixer having a single output, such that, with one syringe holding a precise volume of an isotope mixture at a first concentration and a

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second syringe holding a precise volume of the solvent, driving the plungers of the two syringes simultaneously creates an isotope mixture at the single output of a precise expected concentration less than the concentration of the mixture in the one syringe.

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65. A method for monitoring fluid systems for concentration of selected species, comprising the steps of:

(a) drawing raw samples of the fluid systems one-at-a-time into at least one raw-sample reservoir connected by input fluid conduit to individual ones
10 of the fluid systems;

(b) modifying the raw samples by addition of material from one or more modification modules;

(c) providing measured portions of modified samples to an analytical device; and

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(d) determining concentration of the selected species by the analytical device.

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66. The method of claim 65 wherein, in step (a), there are a plurality of extraction modules associated one-to-one with a like plurality of fluid systems.

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67. The method of claim 66 wherein, in step (a), raw samples are drawn from wet-bath fluid systems in a processing environment, and the extracted fluids are liquids.

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68. The method of claim 67 wherein the wet baths are baths in a semiconductor fabrication unit (fab) devoted to semiconductor integrated circuit (IC) manufacturing.

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69. The method of claim 67 wherein, in step (b), modification is accomplished by adding chemicals for altering pH of extracted liquids.

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70. The method of claim 67 wherein the analytical device is a mass spectrometer, and further comprising a step for vaporizing and ionizing liquids prior to introduction to the mass spectrometer.

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5 71. The method of claim 70 wherein analysis is based on isotopic ratio, and further comprising a step for introducing an isotope mixture to a liquid sample in the system, the isotope mixtures in a ratio not naturally occurring.

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10 72. The method of claim 65, wherein in step (b), additions are made to sample volumes by a fluid handling system through one or more mixers having two or more inputs to one output, the fluid-handling system switching valves between the modules and the inputs to the mixers.

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15 73. The method of claim 72 wherein mixers are implemented as conduit junctions having two or more input conduits feeding one output conduit, with the conduit paths arranged to provide for laminar flow and substantial direction change to influence mixing.

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20 74. The method of claim 65 wherein, in step (a), samples are drawn into the raw-sample reservoir by opening a valve to a vacuum apparatus connected to the reservoir, drawing a relative vacuum in the reservoir to draw material from the fluid system connected by conduit to the reservoir.

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25 75. The method of claim 65 wherein, in step (a), a gas gap is maintained over a liquid sample drawn into the sample reservoir, by implementing the raw-sample reservoir as a vertically-oriented container with conduit from the wet-bath entering at a height on the reservoir above a level anticipated for a sample volume in the reservoir.

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30 76. The method of claim 75 wherein the gas gap is maintained by a cover-gas source connected to the sample reservoir through a remotely-operable valve.

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77. The method of claim 76 wherein the cover gas is nitrogen.

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78. The method of claim 65 further comprising a step for drawing a portion of a raw sample from the sample reservoir via a syringe connected by
5 intermediate conduit to the raw sample reservoir at a height on the reservoir to enter beneath the surface of a sample in the reservoir, such that withdrawing a plunger of the syringe by a precise distance draws a precise volume of the raw sample in the reservoir into the syringe.

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10 79. The method of claim 78 wherein the syringe is operated by a plunger driven through a precision translation mechanism, enabling precision volume control.

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15 80. The method of claim 79 wherein rate of plunger translation is controlled to control rate of fluid transfer.

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20 81. The method of claim 80 wherein the precision translation mechanism comprises a precision stepper motor, and rate of translation is controlled by controlling the stepping rate of the motor..

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82. The method of claim 78 wherein a portion of a raw sample withdrawn into the syringe is ejected to other elements through a three-way switching valve connected to an output conduit.

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25 83. The method of claim 78 further comprising a step for flushing and cleaning the reservoir and the syringe, by operating valves connecting both to a source of cleaning liquid, to a second vacuum source, to a cover-gas source, and to a drain line, and operating these elements to draw cleaning liquid into and through the elements, and then ejecting the cleaning liquid to drain.

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30 84. The method of claim 65 wherein, in step (b), chemicals are added in solution to samples from chemical alteration modules comprising at least one

chemical reservoir having a solution of precisely compounded chemicals and apparatus for providing portions of the solution to the samples.

85. The method of claim 84 wherein chemicals are drawn from the chemical reservoir for addition to samples by a syringe connected by intermediate conduit to the chemical reservoir in a manner to enter beneath the surface of solution in the reservoir, such that withdrawing a plunger of the syringe by a precise distance draws a precise volume of the solution in the chemical reservoir into the syringe.

86. The method of claim 85 wherein the syringe is operated by a plunger driven through a precision translation mechanism, enabling precision volume control.

87. The method of claim 86 wherein the rate of plunger translation is varied, varying thereby rate of liquid movement.

88. The method of claim 86 wherein the precision translation mechanism is driven by a precision stepper motor.

89. The method of claim 85 wherein the chemicals are provided by operating a three-way switching valve connected to the conduit to the chemical reservoir and to an output conduit.

90. The method of claim 89 wherein the portions provided to other elements are provided through a mixer having two or more inputs to one output, with one input connected to the chemical alteration module and another connected to another module in the analytical apparatus.

91. The method of claim 90 wherein individual ones of the mixers are formed of conduit junctions having two or more input conduits feeding one output

conduit, with the conduit paths arranged to provide for laminar flow and substantial direction change to influence mixing.

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92. The method of claim 71 wherein the isotope mixture is provided from one
5 or more isotope dilution modules comprising at least one isotope reservoir containing a mixture of isotopes of a specie to be evaluated, the mixture of isotopes at a ratio not naturally occurring, through a mechanism to provide a portion of the mixture to other elements of the analytical apparatus.

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10 93. The method of claim 92 wherein the portions of the solution are provided via a syringe connected by intermediate conduit to the isotope reservoir below a surface of the mixture in the reservoir, such that withdrawing a plunger of the syringe by a precise distance draws a precise volume of the mixture in the isotope reservoir into the syringe.

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15 94. The method of claim 93 wherein the syringe is operated by a plunger driven through a precision translation mechanism, enabling precision volume control.

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20 95. The method of claim 94 wherein the control and management system is enabled to vary rate of plunger translation.

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25 96. The method of claim 95 wherein the rate is varied by controlling the step rate of a precision stepper motor driving the translation mechanism.

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97. The method of claim 93 wherein the syringe is connected through a three-way switching valve to the conduit to the isotope reservoir and to an output conduit to provide the precise volume sample to other elements of the analytical apparatus.

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30 98. The method of claim 97 wherein the portions provided to other elements are provided through a mixer having two or more inputs to one output, with

one input connected to the isotope dilution module and another input connected to another module in the analytical apparatus.

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99. The method of claim 98 wherein individual ones of the mixers are
5 implemented by conduit junctions having two or more input conduits feeding one output conduit, with the conduit paths arranged to provide for laminar flow and substantial direction change to influence mixing.

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100³. The method of claim 92 wherein isotope mixtures are provided in
10 different concentration levels by maintaining an isotope mixture in a solvent at a specific concentration in the isotope reservoir, and diluting portions of that mixture with solvent from a solvent reservoir, the solvent reservoir containing the solvent common to the isotope mixture in the isotope reservoir, doing the dilution through a system of syringes, connecting conduits and mixers,
15 enabling portions of the isotope mixture to be diluted to lesser concentrations before being provided to other elements of the analytical apparatus.

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101⁴. The method of claim 100 wherein the isotope reservoir holds an isotope mixture in a concentration of 1 part isotope in one million parts of the mixture
20 (1ppm), and the system of syringes, connecting conduits and mixtures enables dilution of six orders of magnitude to one part per trillion (1ppt).

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102⁵. The method of claim 101 wherein individual syringes in the system of syringes are operated by a plunger, such that withdrawing the plunger of the
25 syringe by a precise distance draws a precise volume of the mixture in the isotope reservoir into the syringe.

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103⁶. The method of claim 102 wherein the plunger of an individual syringe is driven through a precision translation mechanism, enabling precision volume
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104. The method of claim 103 wherein the precision translation mechanism is driven by a precision stepper motor.

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105. The method of claim 103 wherein individual ones of the syringes in the
5 system of syringes are connected by switching valves to individual inputs to a mixer having a single output, such that, with one syringe holding a precise volume of an isotope mixture at a first concentration and a second syringe holding a precise volume of the solvent, driving the plungers of the two syringes simultaneously creates an isotope mixture at the single output of a
10 precise expected concentration less than the concentration of the mixture in the one syringe.

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